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SUBSTITUENT EFFECTS ON ^{13}C NMR CHEMICAL SHIFTS IN DIALKYLAMINOPHENYLCHLOROPHOSPHINES

VASILIOS MARATHIAS and MARK M. TURNBULL*

Department of Chemistry, Clark University, 950 Main St, Worcester, MA 01610, U.S.A.

and

ROBERT L. II ABDON and BRIAN P. COPPOLA*

Department of Chemistry, The University of Michigan, Ann Arbor, MI 48109, U.S.A.

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Abstract—The relative chemical shifts and ^2J(PC) coupling constants in the low-temperature limiting spectra of a series of Ph(R_2N)PCl compounds [R = Me, Et, $PhCH_2$, ^{i}Pr and c-Hex] differ for R = primary or secondary. For primary alkyl substituents, the more downfield signal exhibits a large, positive coupling and the more upfield resonance shows a small, negative coupling. These observations are reversed for secondary alkyl substituents. Calculated minimum-energy molecular structures indicate that the source of this reversal does not lie in differences in conformation about the P—N bond. Analysis of the high- and low-temperature limiting spectra of a series of Ph(RR′N)PCl compounds [R, R′ = Me, Et, Bz, ^{i}Pr and c-Hex] suggests that the N—C carbon *syn* to the phosphorus lone-pair is subject to a relatively constant deshielding effect from the phosphorus-lone pair and a shielding contribution from the *anti* substituent that increases with increasing bulk of that *anti* substituent. Conversely, the chemical shift of the carbon *anti* to the phosphorus lone-pair is relatively insensitive to changes in the *syn* substituent, giving rise to the observed chemical shift reversal.

The barrier to rotation about the P—N bond in aminophosphines has been known for some time.[1] Measurements of that barrier have been made in a wide variety of tricoordinate and tetracoordinate phosphines via variable-temperature NMR coalescence techniques.[2] The preferred conformation for these compounds has the nitrogen and phosphorus lone-pairs orthogonal, thus holding one C—N bond *syn*-periplanar and one C—N bond *anti*-periplanar to the phosphorus lone-pair. At low temperature, this results in a pair of doublets in the ^{13}C NMR with different coupling constants. The magnitude and sign of the ^2J(PNC) coupling constants in the ^{13}C NMR spectra of these compounds, observed at sufficiently low temperature to exhibit slow rotation, are dependent upon the dihedral angle between the phosphorus lone-pair and the N—C bond; coupling constants are large and positive when the angle is near 0°, and small and negative when the angle is near 180°.[3,4]

We recently described a correlation between the barrier to rotation about the P—N bond in phenyl (dialkylamino)chlorophosphines, [Ph(R_2N)PCl], and the products of the reaction of the corresponding bis(dialkylamino)phosphine oxides, [$(R_2N)_2P(O)H$], with molybdenum hexacarbonyl.[5] At that time, we noted an unexplained difference in the relative positions of the large and small coupled resonances between compounds bearing methyl or primary alkyl substituents and those having secondary alkyl substituents on the amino group. For small alkyl groups (Me, Et, Bz), the downfield signal exhibited the large coupling constant, while for secondary alkyl groups (^{i}Pr, c-hex) it was the more upfield signal that showed the large coupling constant. The same reversal had been observed earlier.[2f,g] This raised some concerns as to whether the ground state conformations of these molecules

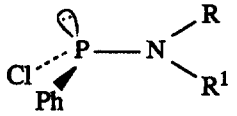
* Authors to whom correspondence should be addressed.

were truly similar, and thus whether our model for describing the phosphine oxide-molybdenum hexacarbonyl reaction was valid. We, therefore, undertook the current study to investigate the source of this chemical shift reversal.

RESULTS

Optimized geometries were calculated for dialkylaminophosphines **1a–f** and **2d** (see Fig. 1). For **2d**, geometries were calculated for both low energy conformers (Bz or Et substituent *syn* to the phosphorus lone-pair). All optimizations showed planar nitrogen atoms and pyramidal phosphorus atoms, regardless of the alkyl substituent. Once the optimized geometries had been calculated, the torsion angle about the P—N bond was set to a series of fixed values for **1a, b, d** and **f** and the molecules were then reoptimized. The calculated torsion angles and observed ^2J(P—C) coupling constants for **1a–f** and **2d** are given in Table 1. A plot of relative energies (normalized to the optimum geometry) vs torsion angle for **1a, b, d** and **f** is shown in Fig. 2.

In addition, a series of dialkylaminophenylchlorophosphines was synthesized where the two N-alkyl substituents were different (**2a–i**). High- and low-temperature limiting ^{13}C NMR {H} spectra, with respect to rotation about the P—N bond, were obtained within the liquid range of the solvent (d_6-acetone, 190–330 K). Chemical shifts and coupling constants of the carbons adjacent to the nitrogen for the low- and high-temperature limiting spectra are given in Table 2, along with those previously reported[5] for compounds **1a–e**. Major and minor conformers were detected for **2a–i** at the low temperature limit. Assignment of those resonances which arose from *syn*-alkyl carbons



1	R = R'	2	R	R'
a	Me	a	Me	Bz
b	Et	b	Me	^{i}Pr
c	Bz	c	Me	c-Hex
d	^{i}Pr	d	Et	Bz
e	c-Hex	e	Et	c-Hex
f	^{t}Bu	f	Bz	^{i}Pr
		g	^{i}Pr	c-Hex
		h	Me	Et
		i	Et	^{i}Pr

Fig. 1.

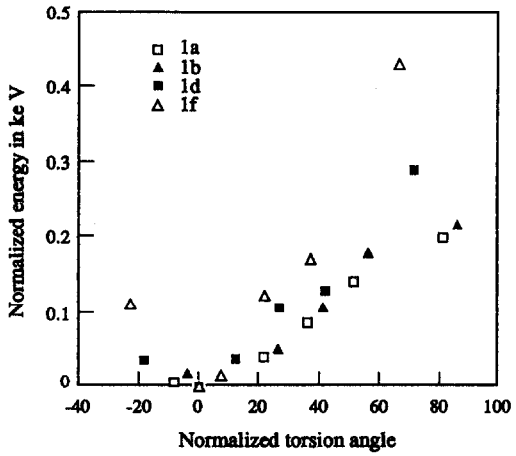


Fig. 2. Relative energies vs torsion angle (both normalized to the optimum geometries) for **1a, b, d** and **f**.

(with respect to the P-lone pair) and those which arose from *anti*-alkyl carbons was made based upon the steric preference of larger substituents to lie in the *syn*-position. The assignments were also made based upon the magnitude of the ^2J(PNC) coupling constants (couplings to *syn*-carbons being significantly larger than those to *anti*-carbons[3]) and were all in agreement with the steric-based assignments. Minor conformer signals for the methyl carbon in **2b, c** were not detected, presumably due to the low population of the conformer and overlap with the solvent resonance. The minor conformer resonance for the methine carbon in **2b** was also

Table 1. Calculated torsion angles (lone-pair P—N—C) and observed coupling constants [^2J(P—C)] for **1a–f** and **2d**

Compound	Calc.	Angle (°)	J_{obs} (Hz)
1a (Me)	*Syn*	35	35
	Anti	152	−13
1b (Et)	*Syn*	35	37
	Anti	150	−13
1c (Bz)	*Syn*	36	36
	Anti	166	−12
1d (^{i}Pr)	*Syn*	29	26
	Anti	154	−13
1e (c-Hex)	*Syn*	26	23
	Anti	158	−12
1f (^{t}Bu)	*Syn*	14	[a]
	Anti	154	[a]
2d (Et)	*Syn*	35	37
(Et)	*Anti*	155	−13
(Bz)	*Syn*	38	40
(Bz)	*Anti*	165	−11

[a] Compound not prepared.

Table 2. ^{13}C NMR chemical shifts[a] of carbon adjacent to N in the R substituent of dialkylaminophenylchlorophosphines [Ph(RR'N)PCl] at high and low temperature limits (*syn* and *anti* to the phosphorus lone-pair) in d_6-acetone as a function of the ancillary substituent R'

	R'				
R	Me	Et	Bz	^{i}Pr	c-Hex
Me HT	40.4(11)	35.6(s)	35.8(s)	30.1(5)	32.5(s)
Syn	42.7(35)	[38.9(36)]	[38.9(34)]	[b]	[b]
Anti	37.2(−13)	33.7(−11)	34.0(−11.5)	28.9(−10)	29.9(−7)
Et HT	49.6(23)	44.7(13)	44.4(11)	42.1(s)	43.5(s)
Syn	50.9(37)	45.9(37)	45.9(37)	[39.5(33)]	[41.4(38)]
Anti	[45.6(−14)]	41.1(−13)	41.4(−12.5)	42.6(−10.5)	43.8(−11)
Bz HT	58.7(24.5)	53.5(14.5)	53.5(12)	51.7(s)	
Syn	59.4(38.5)	55.1(40)	55.3(36)	[49.4(35)]	
Anti	[53.7(−17)]	49.1(−11)	50.1(−12)	51.5(−10.5)	
^{i}Pr HT	55.3(28)	52.8(17)	51.9(15)	49.9(br)	Very broad
Syn	56.4(38)	52.2(27)	50.7(21)	45.1(26)	[46.9(30)]
Anti	[b]	[51.5(−10)]	[52.0(−13.5)]	52.6(−13)	52.4(−10.5)
c-Hex HT	64.3(28)	61.4(18)		Very broad	58.5(br)
Syn	64.4(35)	60.2(23)		53.6(22)	54.9(23)
Anti	[59.0(s)]	[≈60.2][c]		[61.0(−10)]	60.9(−12)

[a] Chemical shifts are in ppm relative to d_6-acetone at 29.8 ppm. Two-bond J(P—C) are given in ( ); negative coupling values have been assigned by convention (see ref. 3). For low-temperature data in compounds with $R \neq R'$, shifts from minor conformers are denoted by [ ].

[b] Minor conformer not detected due to overlap or insufficient population.

[c] Peaks for the minor conformer were not detected. However, based upon the intensities of the peaks for other carbons in the minor conformer, it is unreasonable that these signals would be too weak to detect and thus we conclude that they must overlap the major conformer.

not detected, again for population reasons. A high-temperature limiting spectrum for **2g** could not be obtained below the boiling point of the solvent.

For **2f** {Ph[Bz(^{i}Pr)N]PCl}, assignment of the methylene and methine carbons was not as straightforward. Three peaks were observed at room temperature around 51.8 ppm, two of somewhat lower intensity and one larger one. Because of the significant temperature dependance of chemical shifts,[6] we could not make the assignment based upon the population-weighted chemical shifts of the low temperature resonances. On the other hand, the temperature dependence of the ^2J(PC) coupling constant should be of the order tenths of Hz or less and thus too small to be detected under the same spectroscopic conditions. Calculated values for the methine and methylene couplings, based on the low-temperature coupling constants and relative populations of the two conformers, were 16 and −3 Hz, respectively. The two smaller observed resonances were separated by 15 Hz and thus assigned as the methine doublet. The remaining broad resonance was assigned to the methylene carbon as an unresolved doublet.

Finally, a resonance for the methine carbon in the minor conformer of **2e** was not observed. This was surprising in view of the intensity of the minor conformer resonances of the remaining carbon atoms (signal to noise > 15 : 1). We conclude, therefore, that the methine resonances for the major and minor conformers must be chemical shift equivalent and have assigned the chemical shift for the minor conformer as approximately 60.2 ppm.

DISCUSSION

Modelling studies

Examination of the calculated ground-state conformations of dialkylaminophosphines **1a–f** reveals only minor differences with respect to the P—N torsional angle. The changes in torsion angle about the P—N bond (see Table 1) may be sufficient to account for the reduction in the observed coupling constants from 35–40 Hz for methyl and primary alkyl substituents to 20–30 Hz for secondary alkyl substituents, but clearly is not of a magnitude to account for the observed chemical shift reversal. For substituents *anti* to the phosphorus lone-pair, the differences do not follow this primary/secondary grouping. Torsion angles about other bonds show more significant differences, but these

differences do not vary in a regular fashion as a function of the type of alkyl substituent.

One suggestion for the difference in the magnitude of P—N—C coupling constants (between substituents such as Me and ^{i}Pr) is that it results from differences in conformation about the N—C bonds of the *syn*- and *anti*-alkyl groups, which produces a geared arrangement in the case of the diisopropylamino[2f] substituent (and presumably dicyclohexyl). In this arrangement, the methyls of the *syn*-isopropyl group appear synclinal to the phosphorus atom when viewed along the C—N bond, while the methyls of the *anti*-isopropyl group are anticlinal. The existence of such geared conformations has been demonstrated spectroscopically by Cowley[7] in diisopropylaminotetrafluorophosphorane and crystallographically by Hamor[8] in N,N-diisopropylphenylphosphonamidic chloride.

More encouraging are the calculated barriers to rotation about the P—N bond. As can be seen in Fig. 2, the relative rotational barriers for the dimethylamino (**1a**) and diethylamino (**1b**) compounds are virtually identical, in agreement with the experimental data.[5] As the substitution at the α-carbon increases from primary to secondary (^{i}Pr) to tertiary (^{t}Bu), the barrier increases accordingly, also in agreement with experimental data.[5] Jennings and co-workers have demonstrated the high correlation between such calculated and experimental structures and rotational barriers in a number of related aminophosphine systems.[2g,2i,9]

Analysis of the ^{13}C *NMR spectra*

Based upon the calculated ground state conformations and demonstrated correlation of such calculations with experimental observation, we felt confident that the apparent anomaly, i.e. the chemical shift reversal, was not due to gross changes in the ground state conformation of these molecules about the P—N bond and did not result from changes in the coupling constants. We, therefore, turned towards the idea that changing the degree of substitution of one of the substituents would effect not only its own chemical shift, but that of the other substituent as well. More importantly, we wondered if this effect was different depending upon the position of the substituent. A survey of the literature gave precedence for this effect.

Hargis *et al.* reported the low-temperature limiting ^{13}C NMR spectra of a series of P-dialkylaminodiazaphospholanes.[2f] Their data showed that the *anti*-methyl substituent in 2-dimethylamino-1,3-dimethyl-1,3,2-diazaphospholane was shifted upfield by *ca* 11 ppm when the *syn*-substituent was changed to ^{i}Pr. The chemical shift of the *syn*-isopropyl group in 2-diisopropylamino-1,3-dimethyl-1,3,2-diazaphospholane moved *ca* 6 ppm downfield upon substitution of a methyl group as the *anti*-substituent. Scherer and co-workers did similar studies on P-dialkylaminodiazaphosphasiletidines.[2h] Again, substantial changes in chemical shift were observed for methyl, isopropyl and tert-butyl substituents in either the *syn* or *anti* position when the nature of the *other* group changed.

Encouraged by these observations, we examined the series of mixed alkyl aminophosphines **2a–i** and compared their chemical shifts to those of **1a–e**. Comparison of the high- and low-temperature limiting spectroscopic data for these compounds (Table 2) reveals some distinct trends. In all cases, the chemical shift of the α-carbon of the *syn*-substituent moves upfield 4–5 ppm as the degree of substitution of the *anti*-alkyl group increases from methyl to primary (ethyl or benzyl) to secondary (isopropyl or cyclohexyl). Conversely, with the exception of methyl, the α-carbon of the group *anti* to the phosphorus lone-pair shows little or no change in chemical shift as the nature of the *syn*-substituent is varied. Methyl is unique in this regard, as the chemical shift of the *anti*-methyl group does move significantly upfield with increasing substitution of the *syn*-substituent. The upfield shift observed for the *syn*-substituents, as the *anti*-substituent increases in its degree of substitution, is reminiscent of the "γ-effect" observed in normal alkane chemical shifts for both cyclic and acyclic compounds.[10] If this is the explanation for the observed change in chemical shift with increasing substitution γ to the carbon being viewed, the question becomes one of why the *anti*-substituents *do not* move upfield with increasing substitution of the other group, rather than why the *syn*-substituents do.

Three factors must be considered; the inherent chemical shift of the substituent, the differential shielding effect of the phosphorus lone-pair and the effect of the other N-bonded substituent. Considering the first of these, there is a trend of increasing δ in the order Me < Et < ^{i}Pr ≈ Bz < c-Hex. This is expected based upon the degree of substitution and electronic nature of the groups. This trend is most obvious if one examines the high-temperature limiting chemical shifts for the NR_2 substituted compounds (Table 2).

The differential shielding effect of the phosphorus lone-pair and the effect of the other N-bonded substituent may be conveniently analysed by looking at the change in chemical shift for a given substituent when it moves from the *syn* position to the *anti*

position, as a function of other N-bonded groups. For example, δ_{Me}*syn* is 38.9 and δ_{Me}*anti* is 33.7 ppm when the other substituent is an ethyl group (**2h**). This gives rise to a $\Delta\delta$ Me(Et) value of -5.2 ppm (i.e. the carbon is deshielded in the *syn* position relative to its chemical shift in the *anti* position). The corresponding $\Delta\delta$ values for the remaining substituents as a function of the second N-alkyl substituent are shown in Table 3. The first group has an average $\Delta\delta$ of -5.3 ± 0.4 ppm and is composed primarily of those compounds where both substituents are methyl or primary. The second group has an average $\Delta\delta$ of 1.4 ± 1.5 ppm and is composed of those compounds where one group is primary and one group is secondary. The final group has an average $\Delta\delta$ of 6.6 ± 1.0 ppm and contains the compounds where both alkyl groups are secondary.

These shifts are in good agreement with a combined effect resulting from a constant deshielding contribution from the phosphorus lone pair and a shielding contribution from the other N-bonded substituent that increases with steric bulk, and is dependent upon the position of the group. In the case of the first group, the chemical shift difference for a given substituent in the *syn* and *anti* positions arises only from the differential shielding of the phosphorus lone-pair; the groups are too small to interact significantly. Carbons *syn* to the lone pair are deshielded by 5.3 ppm (±0.4). The one exception to this, **2c**, is the case where one substituent is methyl and the other is cyclohexyl (secondary). If the shielding observed in the other two groups of $\Delta\delta$ values is caused by steric compression (the γ-effect[10]), then we would not expect to see a shielding of the cyclohexyl methine carbon by the methyl substituent as there is no carbon γ to the methine.

The second group of $\Delta\delta$ values, 1.4 ± 1.5 ppm, correlates with those compounds having one primary alkyl group and one secondary alkyl group. Here the substituent in the *syn*-position must be shielded by the *anti*-alkyl group to a greater extent than the deshielding effect of the lone pair. If the lone pair effect is still held to be 5.3 ppm, then the shielding induced by the *anti*-alkyl group must be *ca* 6.5 ppm. It may be that this group can be further subdivided to consider the primary substituents separately from the secondary substituents. It appears from Table 3 that the primary alkyl groups are shielded 1–2 ppm more by the secondary alkyl groups than vice versa, which would also agree with the steric compression argument, but there are too few members of each group to make more than the general observation meaningful.

If the upfield shift of the *syn*-substituent is dependent upon steric congestion, an increase in the value of $\Delta\delta$ in compounds with two secondary alkyl groups should be observed. In **1d**, **e** and **2g**, a carbon *syn* to the lone pair is 6.6 ± 1.0 ppm upfield from its shift in the *anti*-position.

The one question that remains is why there is a pronounced shielding of a carbon in the *syn*-position by the *anti*-substituent, but not the reverse. The explanation may lie in the different steric environments of the two groups. The alkyl group that is *anti* to the lone pair is hindered by *gauche*-like interactions with the P-chloro and P-phenyl substituents. This may force it to adopt a preferred conformation where it is forced into closer proximity with the group *syn* to the lone pair. Conversely, the group in the *syn*-position needs only to compete with the phosphorus lone pair for space and thus can rotate freely about the C—N bond. This reduces its steric effect on the *anti*-group and thus accounts for the observed difference in shielding.

Finally, low-temperature ^{13}C NMR spectra of **2d** indicated a $1 \approx 1$ ratio of the two conformers, based upon relative peak intensities or ^2J(P—C) coupling constants. Calculated minimum energy structures for the two conformers agree with this observation, their energies differing by 0.2 kcal mol^{-1} or less.

Table 3. Change in chemical shift ($\Delta\delta$) required to convert δR_{syn} to δR_{anti} (ppm)

R	(R′)	$\Delta\delta$	R	(R′)	$\Delta\delta$	R	(R′)	$\Delta\delta$
Me	(Me)	−5.5	Et	(^{i}Pr)	+3.1	^{i}Pr	(^{i}Pr)	+7.5
Me	(Et)	−5.2	Et	(c-Hex)	+2.4	^{i}Pr	(c-Hex)	+5.5
Me	(Bz)	−4.9	Bz	(^{i}Pr)	+2.1	c-Hex	(^{i}Pr)	+7.4
Et	(Me)	−5.4	^{i}Pr	(Et)	−0.7	c-Hex	(c-Hex)	+6.0
Et	(Et)	−4.8	^{i}Pr	(Bz)	+1.3			
Et	(Bz)	−4.5	c-Hex	(Et)	≈0			
Bz	(Me)	−5.7						
Bz	(Et)	−6.0						
Bz	(Bz)	−5.2						
c-Hex	(Me)	−5.4						

This implies that these groups, apparently different in size, have similar steric requirements in the present system. We thought that the respective conformational bias energies ("*A* values") of the two substituents on a cyclohexane ring would provide a good comparison of their steric requirements, but were unable to locate such a value for the benzyl substituent in the literature. A comparison of the conformational energies for ethyl and 2,2-dimethylpropyl (*neo*-pentyl),[11] however, shows no difference when measured by the same technique, so the steric near-equivalence of ethyl and benzyl in the present system is reasonable.

In summary, the exchanging of large and small coupled doublets in dialkylaminophenylchlorophosphines observed when the alkyl groups are changed from primary to secondary arises from changes in the relative chemical shifts of the *syn*- and *anti*-α-carbons, not from any significant change in their coupling constants or conformations about the P—N bond. The chemical shifts of the carbons *syn* to the phosphorus lone pair are deshielded by some 5 ppm relative to their shifts in the *anti* position. As the bulk of the substituent *anti* to the lone pair increases, significant shielding of the *syn*-carbon is observed, but the chemical shift of the *anti*-carbon is relatively insensitive to the nature of the *syn*-substituent.

EXPERIMENTAL

All synthetic procedures were carried out using standard Schlenk techniques under an argon atmosphere. Dichloromethane was distilled from CaH_2 and ether was distilled from Na/benzophenone ketyl. All amines were purchased from Aldrich Chemical and used without further purification. $PhPCl_2$ was purchased from Alfa Products and used without further purification. NMR spectra were recorded on a Bruker AC-200 spectrometer (courtesy of the Worcester NMR Consortium) in d_6-acetone solvent and calibrated against TMS (^1H), solvent (^{13}C) or external Ph_3P (^{31}P). ^{13}C and ^{31}P NMR spectra were broad-band proton decoupled unless otherwise noted. Elemental analyses were performed by the University Instrumentation Center, University of New Hampshire, Durham, NH. Compounds **2a**, **c** and **f** have been reported previously.[12] Compounds **2b**, **2d**, **2g**, **2h** and **2i** were hygroscopic oils which hydrolysed rapidly in air. Elemental analyses were not attempted. Compounds **2e** and **2f** were solids and gave satisfactory analyses: For **2e**: Found: C, 61.9; H, 8.0; N, 5.2. Calc. for $C_{14}H_{21}ClNP$: C, 62.3; H, 7.8; N, 5.2%. For **2f**: Found: C, 66.1; H, 6.4; N, 4.9. Calc. for $C_{16}H_{19}ClNP$: C, 65.9; H, 6.6; N, 4.8%.

Ph[Me(Bz)N]PCl (2a)

$PhPCl_2$ (0.52 cm^3, 0.68 g, 3.8 mmol) was dissolved in CH_2Cl_2 (25 cm^3) and cooled to −78°C. N-methylbenzylamine (0.98 cm^3, 0.92 g, 7.6 mmol) was added dropwise over the course of 10 min with vigorous stirring. The reaction mixture was stirred for 4 h, after which time it was allowed to warm to room temperature. The solvent was removed *in vacuo* and Et_2O (50 cm^3) was added. The resulting mixture was filtered and the precipitate washed with 4×15 cm^3 of additional Et_2O. The solvent was removed *in vacuo* from the combined filtrate and washings to give a viscous yellow oil, 1.47 g (92%). ^1H NMR: δ 7.8 (m, 2H, *o*-Ph), 7.5 (m, 3H, *m*- and *p*-Ph), 7.3 (m, 5H, aromatic Bz), 4.2 (d, CH_2, $J = 10$ Hz), 2.4 (d, CH_3, $J = 10$ Hz). ^{13}C NMR: δ 139.9 (d, *i*-Ph, $J = 28$ Hz), 138.2 (d, *i*-Bz, $J = 10$ Hz), 131.2 (d, *o*-Ph, $J = 21$ Hz), 130.8 (s, *p*-Ph), 129.3, 129.2 (two s, *o*-Bz and *m*-Ph), 129.0 (s, *m*-Bz), 127.6 (s, *p*-Bz), 58.7 (d, CH_2 $J = 24$ Hz), 35.8 (s, CH_3). ^{31}P NMR $-\delta$ 148.8.

The remaining compounds (**2**) were prepared by procedures analogous to that for **2a**. Isolated material was characterized by a comparison of physical properties to the literature data where applicable. The broad-band proton decoupled ^{31}P NMR spectra at room temperature, high-temperature limiting ^{13}C NMR and ^1H NMR spectra are reported here for reference.

Ph[Me(^{i}Pr)N]PCl (**2b**) (*colourless oil*, 86%). ^{31}P NMR: δ 141.4. ^{13}C NMR: δ 140.0 (d, *i*-Ph, $J = 28$ Hz), 130.8 (d, *o*-Ph, $J = 20$ Hz), 130.1 (s, *p*-Ph), 129.0 (s, *m*-Ph), 55.3 (d, CH, $J = 28$ Hz), 30.1 (d, NCH_3, $J = 5$ Hz), 21.2 (br s, $CHCH_3$). ^1H NMR: δ 7.7 (m, 2H, *o*-Ph), 7.4 (m, 3H, *m*- and *p*-Ph), 3.7 [d of hept, 1H, CH, ^3J(P—H) = 11.3 Hz, ^3J(H—H) = 6.8 Hz], 2.4 (d, 3H, NCH_3, $J = 8.7$ Hz), 1.2 (d, 6H, $CHCH_3$, $J = 6.7$ Hz).

Ph[Me(c-Hex)N]PCl (**2c**) (*light brown oil*, 93%). ^{31}P NMR: δ 141.9. ^{13}C NMR: δ 140.4 (d, *i*-Ph, $J = 30$ Hz), 131.0 (d, *o*-Ph, $J = 20$ Hz), 130.3 (s, *p*-Ph), 129.1 (s, *m*-Ph), 64.3 (d, CH, $J = 28$ Hz), 32.5 (d, $CHCH_2$, $J = 9$ Hz), 31.9 (d, NCH_3, $J = 5$ Hz), 26.5 (s, $CHCH_2CH_2$), 26.1 (s, $CHCH_2CH_2CH_2$). ^1H NMR: δ 7.7 (m, 2H, *o*-Ph), 7.5 (m, 3H, *m*- and *p*-Ph), 3.2 [d of t of t, 1H, CH, ^3J(P—H) = 12 Hz, ^3J(H—H) = 12 Hz, ^3J(H—H) = 3.5 Hz], 2.4 (d, 3H, NCH_3, $J = 8$ Hz), 1.9–1.0 (overlapping m, 10H, CH_2s).

Ph[Et(Bz)N]PCl (**2d**) (*yellow oil*, 92%). ^{31}P NMR: δ 140.8. ^{13}C NMR: δ 139.8 (d, *i*-Ph, $J = 29.5$ Hz), 138.0 (d, *i*-Bz, $J = 5$ Hz), 131.3 (d, *o*-Ph, $J = 21.5$ Hz), 130.7 (s, *p*-Ph), 129.3 (s, *m*-Ph), 129.1 (d, *o*-Bz, $J = 5$ Hz), 129.0 (s, *m*-Bz), 128.0 (s, *p*-Bz), 53.5 (d, CH_2Ph, $J = 14.5$ Hz), 44.4 (d, CH_2CH_3,

J = 11 Hz), 13.7 (d, CH_3, J = 4.5 Hz). ^{1}H NMR: δ 7.9 (m, 2H, *o*-Ph), 7.5 (m, 3H, *m*- and *p*-Ph), 7.3 (m, 5H, aromatic Bz), 4.3 (d, 2H, PhCH_2, J = 10.3 Hz), 3.0 [d of quar, 2H, CH_2CH$_3$, ^3J(P—H) = 14 Hz, ^3J(H—H) = 7.1 Hz], 1.0 (t, 3H, CH_3, J = 7.1 Hz).

Ph[Et(c-Hex)N]PCl (**2e**) (*light tan solid*, 95%). ^{31}P NMR: δ 136.1. ^{13}C NMR: δ 140.1 (d, *i*-Ph, J = 28 Hz), 131.3 (d, *o*-Ph, J = 22 Hz), 130.3 (s, *p*-Ph), 129.1 (s, *m*-Ph), 61.4 (d, CH, J = 18 Hz), 43.5 (s, CH_2CH_3), 35.2 (d, CHCH_2, J = 7.5 Hz), 34.3 (d, CHCH_2, J = 15 Hz), 26.8 (s, CHCH$_2$$CH_2$), 26.2 (s, CHCH$_2CH_2$$CH_2$), 16.1 (s, CH_3). ^{1}H NMR: δ 7.8 (m, 2H, *o*-Ph), 7.4 (m, 3H, *m*- and *p*-Ph), 3.05 [d of t of t, 1H, CH, ^3J(P—H) = 11.6, ^3J(H—H) = 11.6, ^3J(H—H) = 3.5 Hz], 2.95 [d of quar, 2H, NCH_2, ^3J(P—H) = 14 Hz, ^3J(H—H) = 7 Hz], 2.1–1.1 (several m, 10H, c-Hex CH_2s), 0.92 (t, 3H, CH_3, J = 7 Hz).

Ph[Bz(^{i}Pr)N]PCl (**2f**) (*white solid*, 81%). ^{31}P NMR: δ 133.6. ^{13}C NMR: δ 139.5 (d, *i*-Ph, J = 29 Hz), 139.2 (s, *i*-Bz), 131.5 (d, *o*-Ph, J = 21 Hz), 130.7 (s, *p*-Ph), 129.3 (d, *o*-Bz, J = 4 Hz), 129.0 (s, *m*-Ph), 128.8 (s, *m*-Bz), 127.8 (s, *p*-Bz), 51.9 (d, CH, J = 15 Hz), 51.7 (s, CH_2), 23.8 (d, CH_3, J = 15 Hz), 21.6 (d, CH_3, J = 15.5 Hz). ^{1}H NMR: δ 7.85 (m, 2H, *o*-Ph), 7.4 (m, 3H, *m*- and *p*-Ph), 7.2 (m, 5H, aromatic Bz), 4.2 [AA′ portion of an AA′X pattern, 2H, CH_2, ^3J(P—H) = 7.1 Hz, ^2J(H—H) = 15.2 Hz], 3.4 [d of hept, 1H, CH, ^3J(P—H) = 15.7, ^3J(H—H) = 6.7 Hz], 1.3 (two d, 6H, CH_3s, $J_{app} \approx 6$ Hz).

Ph[^{i}Pr(c-Hex)N]PCl (**2g**) (*white solid*, 77%). ^{31}P NMR: δ 133.8. ^{13}C NMR: δ 140.1 (d, *i*-Ph, $J \approx 29$ Hz), 131.3 (d, *o*-Ph, J = 22 Hz), 130.3 (s, *p*-Ph), 129.2 (s, *m*-Ph), 56.8 (br, $CHCH_2$), 50.8 (d, J = 6 Hz, $CHCH_3$), 36.4, 35.3 (br, CHCH_2s), 27.0 (s, CHCH$_2$$CH_2$s), 26.3 (CHCH$_2CH_2$$CH_2$), 24.0, 23.1 (br, CH_3s). ^{1}H NMR: δ 7.7 (m, 2H, *o*-Ph), 7.4 (m, 3H, *m*- and *p*-Ph), 3.5 [d of hept, 1H, ^3J(PH) = 7 Hz, ^3J(HH) = 6.5 Hz, $CHCH_3$], 3.0 (br m, 1H, $CHCH_2$), 2.0–1.0 (br, 10H, CH_2s), 1.25 (d, 3H, J = 6.5 Hz, CH_3), 1.0 (d, 3H, J = 6.5 Hz, CH_3).

Ph[Me(Et)N]PCl (**2h**) (*light yellow oil*, 98%). ^{31}P NMR: δ 143.8. ^{13}C NMR: δ 140.1 (d, *i*-Ph, J = 28 Hz), 131.1 (d, *o*-Ph, J = 20 Hz), 130.6 (s, *p*-Ph), 129.1 (s, *m*-Ph), 49.6 (d, J = 23 Hz, CH_2), 35.6 (s, NCH_3), 14.0 (d, J = 9 Hz, CH_2CH_3). ^{1}H NMR: δ 7.7 (m, 2H, *o*-Ph), 7.5 (m, 3H, *m*- and *p*-Ph), 3.15 [d of quar, 2H, ^3J(PH) = 10 Hz, ^3J(HH) = 7 Hz, CH_2], 2.55 (d, 3H, J = 10.5 Hz, NCH_3), 1.16 (t, 3H, J = 7 Hz, CH_2CH_3).

Ph[Et(^{i}Pr)N]PCl (**2i**) (*light brown viscous oil*, 79%). ^{31}P NMR: δ 136.4. ^{13}C NMR: δ 140.2 (d, *i*-Ph, J = 30 Hz), 131.3 (d, *o*-Ph, J = 22 Hz), 130.3 (s, *p*-Ph), 129.0 (s, *m*-Ph), 52.8 (d, J = 17 Hz, CH), 42.1 (s, CH_2), 23.6 (d, J = 7 Hz, $CHCH_3$), 22.6 (d, J = 12 Hz, $CHCH_3$), 16.4 (d, J = 6 Hz, CH_2CH_3). ^{1}H NMR: δ 7.75 (m, 2H, *o*-Ph), 7.5 (m, 3H, *m*- and *p*-Ph), 3.55 [d of hept, 1H, ^3J(PH) $\approx$ ^3J(HH) $\approx$ 7 Hz, $CHCH_3$], 2.98 (d of quar, 2H, CH_2CH_3), 1.25 (t, 3H, J = 7 Hz, $CHCH_3$), 1.0 (t, 3H, J = 7.1 Hz, CH_2CH_3).

Molecular modeling

The Sybyl[13] molecular modelling program was used to construct the molecules **1a–f** and **2d**. The geometry of each compound was then fully optimized using MOPAC.[14] This optimization showed planar nitrogen atoms and pyramidal phosphorus atoms regardless of the N-alkyl substituent. Once the optimized geometry had been calculated, the Sybyl program was used to set the torsion angle Cl—P—N—C to specific values (0, 30, 45, 60 and 90°), for **1a**, **b**, **d** and **f**. The geometry was then reoptimized holding the specified torsion angle fixed and the energies of the newly optimized structures were calculated.

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